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STUDIES OF POLYMER ASSOCIATION IN MIXED SOLVENTS

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UNDER CONTRACT Nonr839(02) WITH THE OFFICE OF NAVAL
RESEARCH AND THE POLYTECHNIC INSTITUTE OF BROOKLYN

STUDIES OF POLYMER ASSOCIATION IN MIXED SOLVENTS

-- by --

Riad H. Gebren and H. Morawetz
Institute of Polymer Research
Polytechnic Institute of Brooklyn

Project Number NR 330-029
June 21, 1954
Brooklyn 1, New York

STUDIES OF POLYMER ASSOCIATION IN MIXED SOLVENTS

by

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Association of small molecules and of polymers.

Molecular association in solution is a fairly common phenomenon, but accurate data about the equilibria have been obtained in comparatively few cases. The dimerization of carboxylic acids in non-polar solvents has probably been studied most extensively, and an exhaustive summary of the results was published recently¹. The association of hydroxylic compounds is somewhat weaker, but the dimerization equilibrium can be studied conveniently by cryoscopic measurements².

While the above associations depend on hydrogen bonding, the association complex between e.g. anthracene and trinitrobenzene is due to the polarization of electrons in the aromatic ring system by the dipoles of the nitro groups³. Of a different type is the widespread occurrence of micelles containing a critical number of ions associated in a single kinetic unit existing in equilibrium with molecularly dispersed ions.

It is not surprising, that the same forces responsible for the association of small molecules produce also association complexes of polymers. This accounts for the dependence of the osmotic or light scattering molecular weights of some polymers on solvent medium and temperature^{4,5,6}. In the case of polyvinyl

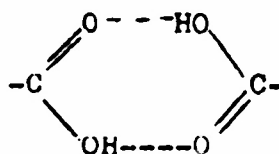
chloride, there is undoubtedly a close relationship between its molecular association and the remarkable mechanical properties of the plasticized polymer⁷.

The surprising feature of these polymer associations is the apparent constancy in the size of the molecular aggregates over a wide range of solution concentration. In this respect the polymer aggregates behave like soap micelles, with the "critical micelle concentration" (i.e., the concentration of incipient micelle formation) apparently well below the lowest concentration at which osmotic, or even light scattering measurements are feasible. The formation of micelles has been interpreted convincingly by Debye's theory⁸ as due to the Van der Waals forces, which favor the clustering of the hydrophobic "tails" of the soap ions and the increasing electrostatic work required to add a further unit to a growing micelle. The free energy of the system goes through a sharp minimum for a given number of ions associated in the micelles, and this explains the narrow distribution of their sizes. It is obvious, that this general reasoning is inapplicable, for example, to the association of polystyrene containing a few hydroxyl groups in toluene solution or a methyl methacrylate-methacrylic acid copolymer in benzene.

Spherical aggregates

To illustrate the problem, let us assume that a flexible coil molecule containing a large number of carboxyl groups may be represented by a sphere, with all carboxyls in the interior

of the sphere dimerized by



and only the carboxyls on the surface of the coil in the free state. When the polymers associate, the aggregate is assumed to be again spherical, with the same density as that of the unassociated macromolecule. For D molecules forming an aggregate, the surface area of the complex will be $D^{2/3}$ times the surface of an isolated coil, and the surface area per macromolecule will be changed by a factor $D^{-1/3}$. Thus, if H_0 is the enthalpy of the unassociated polymer molecules, the dependence of enthalpy H on the degree of association D is given by

$$\frac{\partial H}{\partial D} = - \frac{H_0}{3} D^{-4/3} \quad (1)$$

According to the Flory-Huggins theory^{9,10} the entropy of mixing of polymer and solvent is given approximately by

$$\Delta S = -R \{ N_1 \ln \phi_1 + N_2 \ln \phi_2 \} \quad (2)$$

where R is the gas constant, N the number of molecules, ϕ the volume fraction, the indices 1 and 2 referring to solvent and polymer respectively. As the polymer forms aggregates, the volume fractions remain fixed but the number of independent polymer particles decreases, so that

$$\Delta S = R \left\{ N_1 \ln \phi_1 + \frac{N_2}{D} \ln \phi_2 \right\} \quad (3)$$

and the entropy change with degree of association is

$$\partial S / \partial D = RN_2 \ln \phi_2 D^{-2} \quad (4)$$

The rate of change of free energy with degree of association is then given by

$$\frac{\partial F}{\partial D} = \frac{\partial}{\partial D}(H-TS) = -\frac{H_0}{3} D^{-4/3} - RTN_2 \ln \phi_2 D^{-2} \quad (5)$$

For association to occur, $\partial F / \partial D$ must be negative for $D > 1$, or,

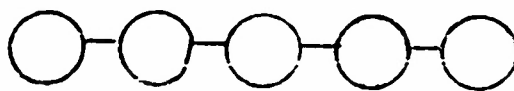
$$\frac{H_0}{3} > -RTN_2 \ln \phi_2 \quad (6)$$

It is apparent, that $\partial F / \partial D$ will then be negative for all values of $D > 1$. Thus the model used leads to the conclusion, that once started, polymer association will continue without limit, i.e. to gelation of the system.

"Pearl necklace model" of polymer aggregates.

This conclusion is clearly contrary to experimental evidence, which indicates that although gelation may occur below a critical temperature, above this temperature the polymers associate to complexes of a size determined by temperature and solvent medium, but insensitive to concentration. This behavior can only be explained by assuming, that due to steric factors and intramolecular association, the "effective functionality" of the polymers, i.e., the mean number of groups available for inter-molecular association, is smaller than 2. The model of the association complex can then be represented

schematically as follows:



The two terminal molecules are linked to one neighbor, while all others are linked twice. The mean effective functionality f_0 is related to the number of molecules in the complex D_0 by

$$f_0 = \frac{2+2(D_0-2)}{D_0} = \frac{D_0-1}{D_0} \quad (7)$$

It can easily be verified, that the same result is obtained if the aggregate has a branched structure, provided only that no closed loops are present,

Polymer aggregates in mixed solvents

If a Lewis base is added to the solution of a polymer containing carboxyl groups, a certain fraction of the carboxyls will associate with the base and the number of groups available for inter-polymer association will decrease. This will cause a reduction in the apparent molecular weight of the polymer. The association equilibrium of acid A and base B is given by

$$\frac{(AB)}{(A)(B)} = K \quad (8)$$

and the ratio of the total concentration of acid groups to the concentration of acid groups remaining free in the presence of added base is

$$\frac{(AB) + (A)}{(A)} = 1 + K(B) \quad (9)$$

It is reasonable to postulate, that the effective functionality f of the polymer in a solution containing base

will bear the same relation to the functionality f in the absence of base as the concentration of acid groups unassociated with the base to the total acid group concentration. Utilizing equation (7) and (9)

$$\frac{f_0}{f} = \frac{D_0-1}{D-1} \cdot \frac{D}{D_0} = \frac{(AB)+(A)}{(A)} = 1 + K(B) \quad (10)$$

Thus, the dependence of the degree of association on the concentration of added base should yield information from which the association constant K can be calculated.

Experimental Results

In a previous publication the molecular associations were investigated for mixtures of methyl methacrylate copolymers with methacrylic acid and dimethylaminoethyl methacrylate, respectively¹¹. It was found, that association of the acid copolymer competes strongly with the carboxyl-amine interaction. Also, the importance of any carboxyl association with the ester groups of the copolymers was quite uncertain.

To determine the relative contributions of the different types of association to the formation of the polymer aggregates, the apparent osmotic molecular weight of a methyl methacrylate-methacrylic acid copolymer in benzene solution was measured as a function of added dimethylaminoethyl acetate (DAEA), ethyl acetate, acetic acid and butanone. The copolymer contained 4.9 mole % methacrylic acid (determined by titration with sodium ethoxide in 90 volume % benzene and 10 volume %

ethanol) and its number average molecular weight (measured in pyridine solution, where polymer association cannot take place) was 34,500. The osmotic pressure measurements were carried out as described previously¹¹ at a temperature of 29.8°C. In benzene solution, the degree of association D_0 was found to be 6.86.

The results obtained are listed in Table 1 and plotted in Figure 1. Dimethylaminoethyl acetate and ethyl acetate addition reduced the degree of association of the polymer in the expected manner, and the slopes of the plots of $(D_0-1)D/(D-1)D_0$ against (B) lead to association constants of 86 liters/mole and 6.7 liters/mole respectively. Butanone was relatively inefficient in reducing the degree of polymer association, thirty times as much of it being required to produce the same effect as methyl acetate. While the ester carbonyl would be expected to be more basic than the carbonyl of the ketone, the magnitude of this difference is surprising.

The interpretation of data obtained in solutions to which acetic acid was added is more complex. The acid is largely dimerized, but the monomeric form is chiefly responsible for any interaction with the polymer. The dissociation constant of acetic acid dimer in benzene at 29.8°C. was estimated from published data¹² to be 6.6×10^{-3} moles/liter, and the values of (B) used in Figure 1 refer to the calculated concentrations of the monomeric acid. It can be seen that the plot of $(D_0-1)D/(D-1)D_0$ against (B) is strongly curved in this

case. This is ascribed to the fact, that the monomeric acetic acid associates both with carboxyl and with ester groups of the polymer. In addition, the possibility cannot be excluded that there is some hydrogen bonding of carboxyl with the acetic acid dimer.

Conclusion

It is concluded, that in the acid copolymer used in this and the previous investigation¹¹ most of the aggregation is due to carboxyl-ester association. Also, since the carboxyl-amine association constant is only 13 times as high as the association constant of carboxyl with ester groups, a methacrylate copolymer containing 5 mole % of amine groups would owe somewhat more of its association with a carboxylic polymer to carboxyl-ester than to carboxyl-amine interaction. The method outlined is believed to be a useful tool in determining a variety of association constants, with a possible bearing on the theory of polymer solubility and plasticization¹³.

TABLE 1.

Association of methyl methacrylate-methacrylic acid copolymer
in benzene at 29.8°C. in the presence of various additives.

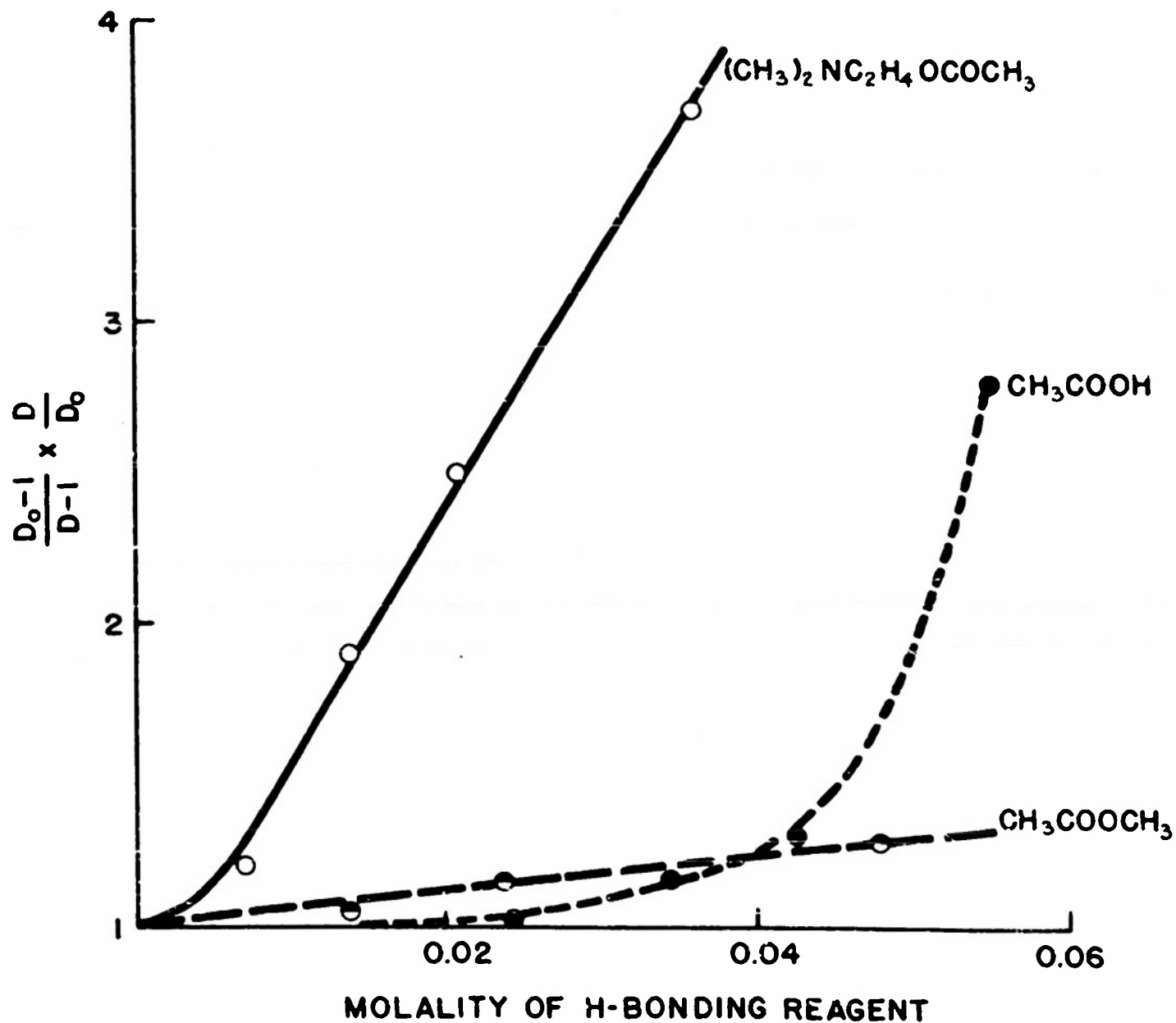
<u>Additive</u>	<u>(B)</u>	<u>D</u>	$\frac{D_0-1}{D-1}$	$\frac{D}{D_0}$
DAEA	0.0062	3.62	1.18	
DAEA	0.0124	1.82	1.89	
DAEA	0.0186	1.52	2.50	
DAEA	0.0310	1.30	3.70	
Methyl acetate	0.012	5.54	1.04	
Methyl acetate	0.021	4.22	1.12	
Methyl acetate	0.042	2.98	1.28	
Butanone	0.553	4.23	1.12	
Acetic Acid (*)	0.0213	5.96	1.03	
Acetic Acid	0.0303	3.84	1.15	
Acetic Acid	0.0375	2.90	1.30	
Acetic Acid	0.0480	1.44	2.80	

(*) Concentrations in monomeric
 acetic acid.

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EFFECT OF ADDITIVES ON THE DEGREE OF ASSOCIATION
OF METHYL METHACRYLATE-METHACRYLIC ACID CO-
POLYMER IN BENZENE.



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